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Heavy metals and their impact on environment at the dump-field Ľubietová-Podlipa (Slovakia)

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1. Introduction

The Ľubietová deposit was exploited since the time of the Bronze Age and in the 16th and 17th centuries it was one of the most important and most extensively exploited Cu-mines of Europe. The Cu-ore was in the 18. century exported to more than 50 countries (Koděra et al. 1990).

The Cu mineralisation with Ag admixture is developed within 4 – 5 km long and 1.5 km wide range of N-S direction. There are three main ore-fields in the Ľubietová surrounding: Podlipa, Svätodušná and Kolba with admixture of Co/Ni-mineralisation. The Cu content in the ore ranged from 4 – 10 % and the Ag content was about 70 $g.t^{-1}$ (Koděra et al., 1990). 25 thousand tons of Cu were exploited during last five centuries.

The main dump-field Podlipa represents about 2 km^2 area and was exploited by 18 adits. The ore mineralisation is situated in the Ľubietová terrigene crystalline complex of Permian age which consists of greywackes, arcose schists and conglomerates. The main tectonic structures are of NE-SW direction, the main ore veins strike approximately E-W and N-S. Ore veins are 30 – 40 m thick. In the southern part of the ore-field was described also disseminated mineralisation.

The probably volcano-sedimentary mineralisation, genetically connected with the basic, intermediate and acid Permian volcanism, was mobilised by Hrončok granite intrusion during the Alpine (upper Cretaceous) orogene (Ebner et al., 2004). The vein mineralisation is characterised by a rather simple paragenesis which is represented by quartz, siderite, (± calcite and ankerite), chalcopyrite, Ag-bearing tetrahedrite, arsenopyrite, pyrite, barite and rare galena. In the well developed cementation zone the main Cu-minerals were cuprite and native copper. The deposit is famous also because of formation of wide range of rare secondary minerals as libethenite, langite, annabergite, aurichalcite, azurite, brochantite,

cyanotrichite, erithrine, evansite, euchroite, farmacosiderite, hemimorphite, chrysocol, cuprite, limonite, malachite, olivenite, tirolite, pseudomalachite, copper etc. (Koděra et al. 1990).

Although the intensive mining activities were stopped during the 19th century (the last owner of the mine near Haliar locality Ernest Schtróbl finished the exploitation during the WWI on April 1915 because of the limited number of the miners) and only a few geological survey activities with negligible effect have been carried out here since, the area remains substantially affected.

2. Experimental

The samples (of about 30 kg weight) of sediments from the dumps and soil from the 30 – 50 cm depth (the sampling step was 25 m^2), surface water (stream water, drainage water) and groundwater were collected for the characterisation of landscape components contamination. The reference site was selected for comparison of territories loaded by heavy metals and non-contaminated natural environment (Figure 1). It was situated outside of geochemical anomalies of heavy metals and represents graywakes of Permian age, similar to material at the dump-field. The samples of plant material were collected both from the reference area and from the contaminated dumps.

The dump-sediments are represented by two sets of samples: the first one consists of 15 samples (samples HD-1 to HD-15) and the second one of 15 samples (A-1 to A-15). Samples HD-10, HD-11 and A-12 represents the reference area. The sample set is completed by sample of limonitised rock (A-17), which represents mixture of three samples from localities A-2, A-3 and A-5.

The water samples were collected during the dry seasons (February 25th 2007 and May 27th 2008) and wet seasons (June 14th 2006 and March 31st 2008). To the each sample of 1 000 ml volume was added 10 ml of HCl.

Vegetation creates small isles and is enrooted in few depressions which have enabled limited soil-forming process. The selection of plant species was performed so that it could be possible to compare all identical plant species from the contaminated planes with plants from the reference sites. The samples of hardwood species (*Betula pendula, Quercus petraea, Salix fragilis*), coniferous species (*Pinus sylvestris, Abies alba, Picea abies*) and herbs (*Juncus articulatus, Mentha longifolia*) were studied. At everyone site were sampled 10 individuals of each plant species to get average sample. Five coniferous individuals of approximately same age were sampled for branches (in case of *Picea abies* also needles) from the fourth or fifth spike with approximate length of segment from 10 to 15 cm. In the case of *Pinus sylvestris* were analysed two years old needles. Roots of the same length and with 2 - 3 cm diameter were obtained from the surface soil level. Similar mode of sampling was used at hardwood species: 3 – 4 years old branches were sampled from the lower limbs. The samples were dried at laboratory temperature and then homogenized.

The clay mineral fractions from 8 samples (A-1c to A-11c and A-17c) of technogenous sediments were prepared according to the method described by Šucha et. al. (1991). To remove carbonates from the sample pulverised to <0.16 mm grain size, is to the 10 g of sample added 100 cm^3 of natrium acetate buffer. Reacted solution is after 2 days segregated from the solid phase and the solid phase is dispersed by SOTR addition in ultrasound

device during 2 – 3 minutes. The sample is three times heated up to 90 °C with 100 cm^3 SOTR addition and the suspension is decanted.

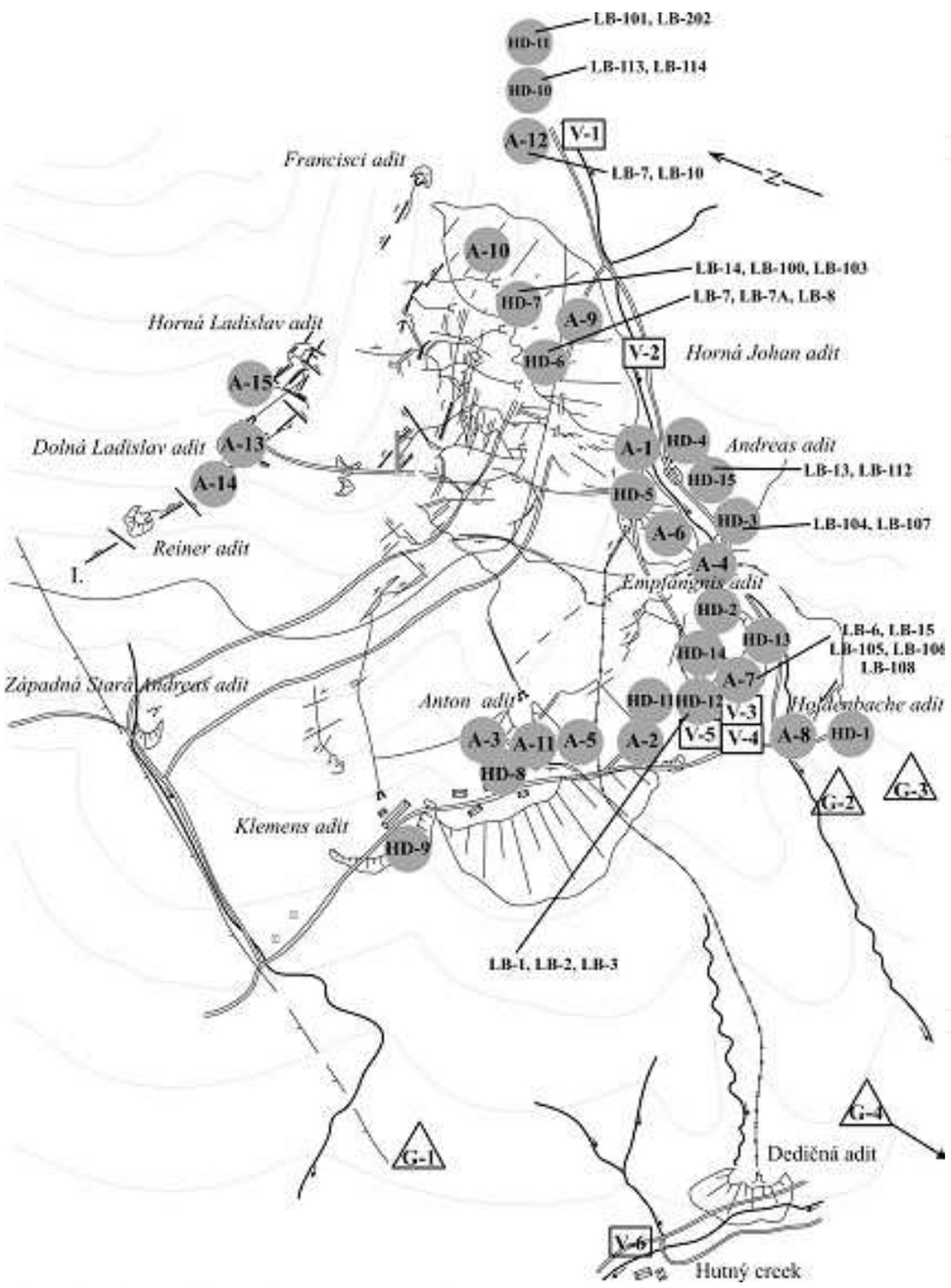

Fig. 1. Localisation of the technogenous sediment, water and plant samples

Organic mater was removed by reaction with 10 cm^3 of concentrated hydrogen peroxide and 100 cm^3 of SOTR. The mixture was heated at 70 °C 15 minutes. This proceeding was two times repeated and the reacted solution was removed.

The free Fe and Mn oxides are removed by addition of 90 cm^3 citrate solution and by heating up to 75 – 85 °C. After 5 minutes double additions of 2 g of natrium hydrosulphite was realised and the solution was decanted. The rest of the sample was irrigated by distilled water.

After mentioned procedure is possible to realise the true separation of clay minerals (<2 μm fraction). The coloidal rest of the sample in 2 dm^3 of distilled water is after 41 hours and 8 minutes (the time is calculated according to Stokes rule for gravitation sedimentation) decanted to beaks and saturated solution of NaCl is added. After treating is the solution fleeced. The solid rest is transposed to calciferous form using 1 $mol.dm^{-3}$ $CaCl_2$ solution. This procedure regulate the replacable cations in clay minerals. Dialysis is sused for chlorides removal and the presence of chlorides is verified by additament of $AgNO_3$ solution. After removing of chlorides is the rest of the sample drained at 30 °C.

To the 0,14 g of sample was added 3,5 cm^3 of distilled water and using ultrasound was the sample dispergated. Suspension was applied using syringe on mount glass and was drained at laboratory temperature to get oriented mount. These oriented mounts were saturated by ethylenglycol gasses in exicator during 8 hours on ceramic skid at 60 °C to optimise the conditions of the rtg-diffraction analysis.

Rtg-diffraction analyses of clay minerals were realised in the laboratories of the Geological Institute of the Slovak Academy of Sciences using X-ray difractograph PW 1710 Philips (analysed RNDr. Ľubica Puškelová).

The existence of clay mineral free sorption capacity was studied using heavy metals containing drainage water from terraine depression beneath the dump of the Empfängnis adit. To 20 g of clay sample (A-1c to A7c and A-17) was added 50 cm^3 of 5-times concentrated drainage water. Analyses were realised from 1 g of sample (A-1* to A7* and A-17* after 14 days maceration in drainage water.

Rinse pH of the sediments was measured in the mixture of distilled water and unpulverised sample (Sobek et al., 1978). The pH of the sediments was determined also from mixture of unpulverised sediment and 1M KCl according to Sobek et al. (1978). In both eventualities to 10 g of sediment sample 25 ml of distilled water or 1M KCl was added and after two hours of mixing in laboratory mixer the pH and Eh was measured.

The samples of technogenous sediments from the dumps and soils were dried and 0.25 g of sample was heated in HNO_3-$HClO_4$-HF to fuming and taken to dryness. The residue was dissolved in HCl. Solutions were analysed by ICP-MS analyse in the ACME Analytical Laboratories (Vancouver, Canada). Plant samples were divided into roots, branches/stems, leaves/needles and flowers/fruits. 0.5 g of vegetation sample was after split digestion in HNO_3 and then in Aqua Regia analysed by ICP-MS for ultralow detection limits. The contamination of live and dead parts was compared in several plants. Plants were analysed in the same laboratory as sediments.

The carbon content (total carbon – $C_{tot.}$, organic carbon - $C_{org.}$ and inorganic carbon $C_{inorg.}$) was determined in the laboratories of the Geological Institute of the Slovak Academy of Sciences by IR spectroscopy using device Ströhlein C-MAT 5500 (analysed Alžbeta Svitáčová).

The water samples were analysed using AAS in the National Water Reference Laboratory for Slovakia at the Water Research Institute in Bratislava. The speciation of As was performed on the basis of different reaction rate of As^{3+} and As^{5+} depending on pH (analysed Ing. Adriana Shearman, PhD).

The efficiency of the Fe^0-barrier for heavy metals removal from the surface water was tested in the laboratories of the Faculty of Natural Sciences at the Comenius University in Bratislava (Mgr. Bronislava Lalínska).
Microscopical analyses of plant tissues were realised in the laboratories of the Department of Wood Science of the Technical University Zvolen (analysed Ing. Miroslava Mamoňová, PhD).

3. Results

3.1 Heavy metal contamination of the technogenous sediments

The dump-field sediments are influenced by heavy metals from the hydrothermal Cu-mineralisation. The main contaminants: Fe (up to 2,64 %), Cu (25 ppm - >10 %), Mn (34 - 1258 ppm), As (7 - 289 ppm), Pb (8 - 130 ppm), Co (5,1 - 96,3 ppm), Sb (7 – 62 ppm) and Ni (7,8 - 62,1 ppm) are accompanied also by U (up to 10 ppm) and Th (up to 35 ppm).

El.	Unit	Sample											
		A-1	A-1c	A-1*	A-2	A-2c	A-2*	A-3	A-3c	A-3*	A-4	A-4c	A-4*
Fe	%	1.31	1.45	2.98	1.42	1.46	2.17	1.94	2.14	2.90	2.64	2.47	3.65
Cu	ppm	2829	1693	2345	199	574	472	828	624	857	4471	3324	3112
Pb		28	64	229	130	22	28	16	23	37	10	15	38
Zn		14	18	95	21	36	62	20	25	47	23	16	27
Cd		<0.1	<0.1	0.2	0.1	0.2	0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1
Bi		2.8	4.5	14.6	0.2	1.4	1.5	8.5	7.2	12.1	23.7	39.2	90.9
Co		10.4	11.3	18.3	5.9	10.3	6.4	14.0	17.0	11.0	50.0	58.3	32.1
Ni		36.8	36.0	71.8	9.8	12.2	17.0	32.1	28.3	30.4	55.0	42.4	64.4
As		162	258	628	10	19	15	71	110	105	169	237	300
Sb		62	60	153	7	9	13	22	24	28	59	79	130
Ag		0.7	0.8	1.7	<0.1	0.1	0.2	0.4	0.6	0.9	1.4	2.1	4.1
Cr		38	9	24	36	17	26	34	21	37	38	15	30
Sn		10.9	11.1	29.4	3.5	2.7	4.4	9.8	7.2	9.5	17.3	12.8	22.7
U		1.3	1.4	3.3	1.4	1.1	1.1	1.7	1.8	1.9	1.6	1.7	2.2
Th		5.8	6.0	9.5	7.6	5.9	2.2	9,1	9,2	5,2	8,3	7,8	5,0

Table 1. ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water. Explanation to tab. 1 and 2: A-1 to A-12 technogenous sediments, A-1c to A-10c clay fraction; A-1* to A-10* clay fraction after 14 days maceration in drainage water; A-17 hydrogoethite rich rock

The heavy metal distribution in technogenous sediments of the dump-field is variable (tabs. 1 – 4). The distribution of individual elements reflect the primary concentration in separate parts of the dump-field as well as their geochemical relations (figs. 2 – 7), first place their migration ability. In general we can distinguish at the dump-field three types of heavy metals: 1. group: Fe, Cu (figs. 2 and 3), As, Sb, Sn, Co, Ni, Cr, Ag, V, U, Th (figs. 4 and 5); 2. group: Zn, Bi, Cd (Figure 6); 3. group: Pb (Figure 7).

El.	Unit	Sample											
		A-5	A-5c	A-5*	A-6	A-6c	A-6*	A-7	A-7c	A-7*	A-8	A-8c	A-8*
Fe	%	1,71	1,66	1,83	2,06	2,09	3,36	1,32	1,43	2,81	0,91	1,29	0,79
Cu	ppm	3150	3001	2078	4797	2503	2918	756	855	2026	716	836	837
Pb		17	15	22	16	25	72	17	20	74	7	6	4
Zn		19	18	45	13	14	65	26	33	176	7	14	4
Cd		<0,1	<0,1	<0,1	0,2	<0,1	0,3	<0,1	0,2	0,7	<0,1	<0,1	<0,1
Bi		1,7	2,1	3,2	25,4	24,4	51,7	0,9	1,2	3,6	0,5	0,7	0,8
Co		24,4	30,4	29,6	41,8	40,9	32,0	10,2	12,0	15,5	89,9	69,7	104
Ni		34,0	34,1	55,4	51,6	45,1	61,7	10,4	10,1	26,0	58,0	66,5	62,5
As		60	64	105	134	224	305	16	17	33	61	52	46
Sb		17	16	30	50	56	92	12	7	17	18	20	19
Ag		0,1	0,1	0,2	1,0	1,6	3,0	0,2	0,2	0,4	<0,1	<0,1	0,1
Cr		30	10	22	31	11	23	28	11	35	23	21	7
Sn		4,9	3,3	8,1	14,9	12,9	19,6	4,0	2,6	6,8	3,9	7,1	3,0
U		1,0	1,2	1,4	1,4	1,6	2,2	1,1	1,1	2,3	2,6	2,5	2,1
Th		5,9	5,8	4,0	6,9	6,1	4,1	4,8	5,3	11,8	6,8	5,7	6,7

Table 2. ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water.

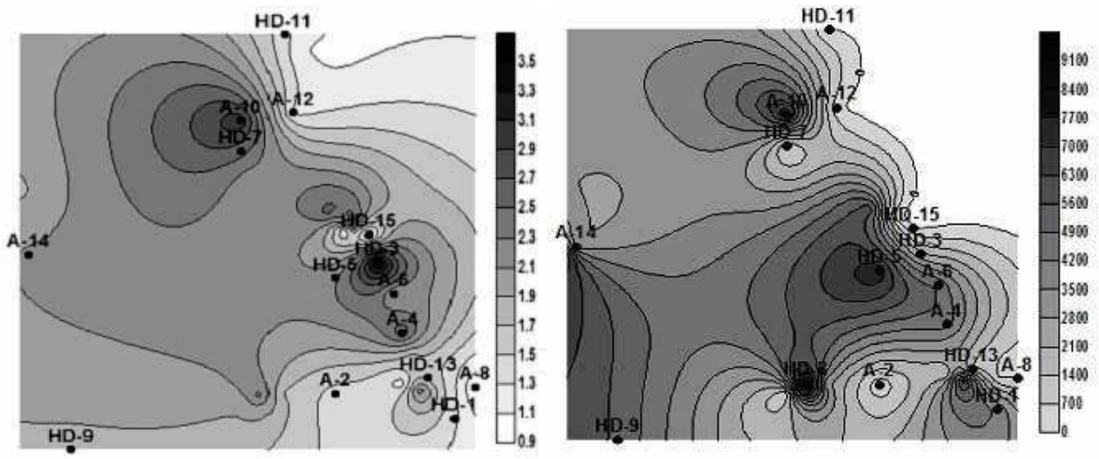

Fig. 2 and 3. Distribution of Fe and Cu at the dump-field Ľubietová (explanation to figs. 2 – 7: the numeric indexes represtent the concentration of heavy metals in % or ppm)

Element	Unit	A-9	A-9c	A-9*	A-10	A-10c	A-10*
Fe	%	1.84	2.14	5.03	1.12	1.66	2.03
Cu	ppm	5466	3112	1181	390	231	176
Pb		18	23	41	54	60	74
Zn		24	25	31	36	40	52
Cd		0.1	0.1	0.2	0.3	0.2	0.4
Bi		8.1	10.2	15.4	1.7	2.8	4.1
Co		96.3	98.2	98.2	7.1	8.3	7.9
Ni		51.9	48.6	62.7	7.8	6.3	9.7
As		130	148	234	32	47	76
Sb		28	37	48	18	28	47
Ag		0.6	0.7	1.3	0.3	0.5	0.9
Cr		11.8	8.7	9.9	12.5	7.5	9.6
Sn		12.1	10.2	15.8	4.1	3.7	4.8
U		2.1	2.3	2.7	1.1	1.2	1.3
Th		8.8	8.1	7.2	6.4	5.4	4.7

Table 3. ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water.

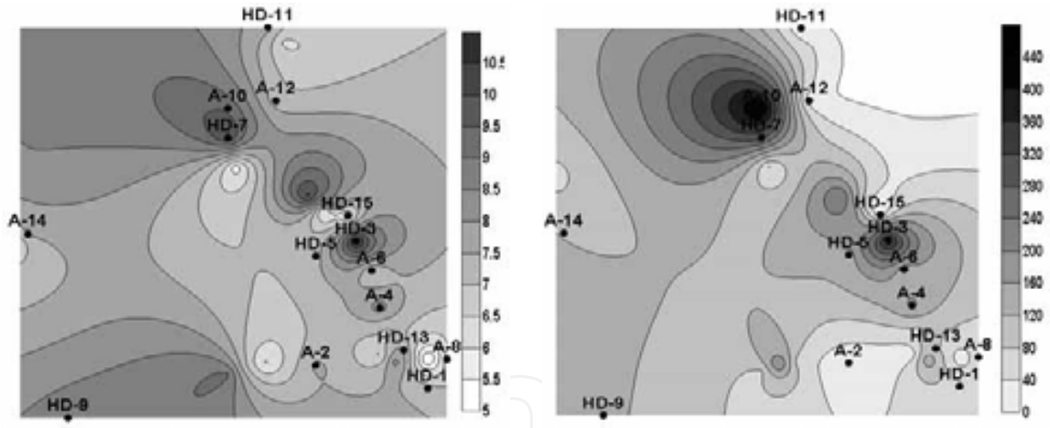

Fig. 4 and 5. Distribution of Th and As at the dump-field Ľubietová

3.1.1 Total Acidity Production (TAP) and Neutralization Potential (NP)

The indirect indicator of oxidation are hydrogoethite and gypsum. The oxidation of sulphide minerals is indicated also by coating of secondary oxides and Cu-carbonates. The less oxidised is the fine grained pellitic material. The direct indicator of oxidation processes is the pH.

To determine the Total Acid Production (TAP) and the Neutralisation Potential (NP) is necessary to know the Eh and pH values of the sediments (in distilled water and in 1M KCl lixivium) as well as the carbon and sulphur content. If distilled water is used in the measurment of paste or rinse pH, its pH is typically around 5.3. Consequently, any pH

measurment less than 5.0 indicates the sample contained net acidity. Carbonate minerals can create pH values around 8 – 10 and thus values above 10 are usually alkaline. Values of paste pH between 5 and 10 can be considered near neutral (Sobek et al., 1978).

Element	Unit	A-11	A-11c	A-11*	A-12	A-17	A-17c	A-17*
Fe	%	2.37	3.02	4.44	1.38	1.72	1.50	13.10
Cu	ppm	>10 000	8 756	7654	25	>10 000	20 360	23 060
Pb		14	24	33	16	8	49	60
Zn		15	17	21	39	59	80	50
Cd		0.1	0.1	0.2	0.2	0.2	0.2	0.2
Bi		2.6	3.2	4.7	0.2	7.2	6.0	5.0
Co		84.5	77.5	85.1	5.1	73.4	70.0	83.0
Ni		62.1	59.8	64.1	8.5	51.7	43.0	58.0
As		206	211	243	7	289	260	280
Sb		36	38	40	10	43	40	34
Ag		1 258	1 322	1 452	559	1 074	960	1 010
Cr		0.7	0.8	1.7	0.3	2.2	2.0	30.0
Sn		<1	<0.1	<0.1	<1	<0.1	<0.1	<0.1
U		0.3	0.4	0.6	0.1	0.8	1.0	1.0
Th		29	25	31	31	15	16	15

Table 4. ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water.

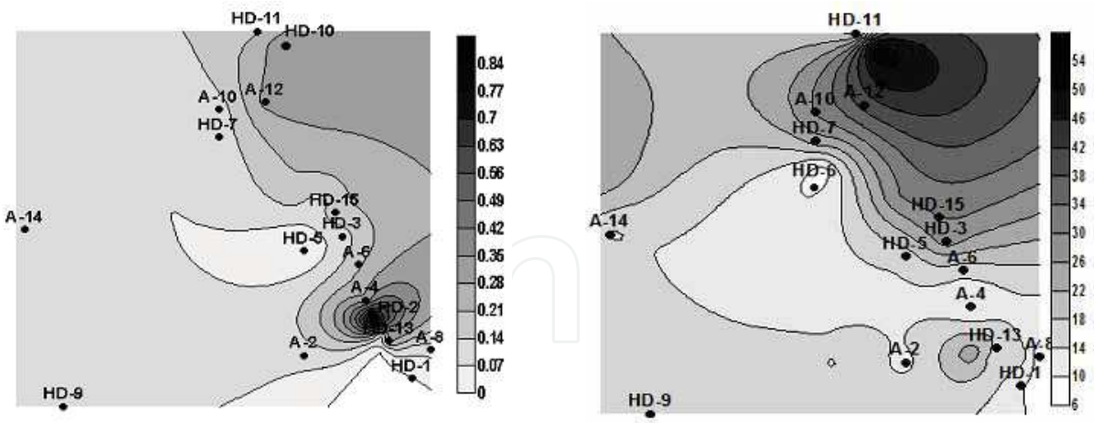

Fig. 6 and 7. Distribution of Cd and Pb at the dump-field Ľubietová

The pH values in sediments measured at the dump-field in the distilled water lixivium range from 4.21 to 7.93 (tab. 5). It is interesting, that the lowest pH value was determined in the samples from reference area. It is caused probably by the fact, that in spite of absence of sulphides there are no carbonates; the carbon content is very low ($C_{tot.}$ 0.40 %, $C_{org.}$ 0.37 %

and concentration of the inorganic carbon $C_{org.}$ is below the detection limite (tab. 5). The highest carbon content is in sample A-7 ($C_{tot.}$ 1.63 %; re-counted for $CaCO_3$ even 12.71 %).
The samples contain 0,01 – 0,42 % of total sulphur (tab. 5). The highest content of total sulphur is in the sample A-6 from the Empfängnis adit, where the sulphidic sulphur (S_S 0.27 %) prevalence on sulphate sulphur (S_{SO4} 0.15 %) was recognised. At the dump-field Ľubietová in the majority of the samples is dominant the S_{SO4} vs. S_S thus in the dump material still contain a great portion of not oxidised sulphidic minerals. According to Sobek et al. (1978) the calculation of the TAP value is possible by multiplication of the $S_{tot.}$ (or S_S) content by coefficient 31.25, which is derived from the neutralisation equation:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$$

This datum is equal to quantity of acid which could be potentially produced by the dump material. At Ľubietová – Podlipa dump-field range the TAP value from 0,3125 to 13,125 (in average 3,7; tab. 6). The highest TAP values are at the dump of the Empfängnis adit and the lowest at the little dump of Holdenbachen adit beneath the wooded slope of the Zelená Dolina Valley (Figure 1).

Sample	H_20		1M KCl		%							
	pH	Eh (mV)	pH	Eh (mV)	$S_{tot.}$	S_{SO4}	S_s	$C_{tot.}$	$C_{org.}$	$C_{inorg.}$	CO_2	$CaCO_3$
A-1	5.14	77	4.61	109	0.25	0.10	0.15	0.74	0.20	0.54	1.97	4.48
A-2	5.89	34	5.40	63	0.02	0.01	0.01	0.86	0.38	0.48	1.75	3.99
A-3	4.87	94	4.21	131	0.10	0.03	0.07	0.62	0.34	0.28	1.02	2.32
A-4	5.46	59	5.33	66	0.33	0.13	0.01	0.34	0.26	0.08	0.29	0.66
A-5	5.77	42	5.37	64	0.05	0.01	0.05	0.78	0.35	0.43	1.57	3.57
A-6	5.17	74	5.06	83	0.42	0.15	0.27	0.40	0.27	0.13	0.47	1.08
A-7	7.93	-84	7.34	-58	0.03	0.02	0.01	1.63	0.10	1.53	5.61	12.71
A-8	5.42	36	5.22	42	0.01	0.01	0.01	0.45	0.13	0.32	1.17	2.66
A-9	5.03	83	5.01	85	0.03	0.03	0.01	0.40	0.37	tr.	tr.	tr.
A-10	5.25	71	5.14	78	0.04	0.02	0.02	0.48	0.46	tr.	tr.	tr.
A-11	6.11	22	5.95	30	0.11	0.04	0.07	4.31	4.18	0.13	0.47	1.08
A-12	4.21	133	3.47	173	0.02	0.01	0.02	4.05	4.03	tr.	tr.	tr.

Table 5. Characteristic of the samples of technogenous sediments from dump-field

To define the risk of the acidity production it is necessary to know also the neutralisation potential (NP), which define the content of the neutralisation matter in the dump-field able to neutralise the dump produced acidity. The distribution of NP values within the individual parts of the Podlipa dump-field show substantial differencies (from 0 to -127.1, in average 27.1; tab. 6) and it is more or less in negative correlation to the Total Acid Potential (TAP). For example to the TAP 13.125 value (in sample A-6 where the highest $S_{tot.}$ 0.42 % and S_S 0.27 % contents were described; tab. 5) rises value NP 10.8, while to the lowest TAP value 0.3125 (sample A-8) rises NP 26.6. Higher NP – 127.1 is only in the sample A-7 (tab. 6), where the highest $C_{tot.}$ was appointed (equal to 12.71 kg.t^{-1} $CaCO_3$; tab. 5).

The Net Neutralisation Potential (NNP) is equal to the quantity of neutralisation matter (usually n.kg $CaCO_3$ per 1 ton of material), necessary for neutralisation of dump-field matter produced acidity (NNP = NP – TAP). NPP values at the Podlipa dump-field are presented in tab. 6. The results show that to neutralise the dump material it would be necessary use such a quantity of neutralisation reagent which is in average equal to 23.5 kg $CaCO_3$ per 1 ton of dump matter. The risk of the Acid Mine Drainage water (AMD) formation is best expressed by NP:TAP ratio. If it is close to value 1, the risk of the AMD formation is highly feasible. In case when the mentioned ratio is equal to 3 or >3, the risk of the AMD formation is negligible (Sobek et al., 1978).

Sample	TAP	NP	NNP	NP:TAP
A-1	7,81	44,8	37,0	5,7
A-2	0,62	39,9	39,3	63,8
A-3	3,12	23,2	20,1	7,4
A-4	10,31	6,6	-3,7	0,6
A-5	1,56	35,7	34,1	22,8
A-6	13,12	10,8	-2,3	0,8
A-7	0,93	127,1	126,2	135,6
A-8	0,31	26,6	26,3	85,1
A-9	0,93	0	-0,9	0,0
A-10	1,25	0	-1,3	0,0
A-11	3,43	10,8	7,4	3,1
A-12	0,62	0	-0,6	0,0
Mean	3,7	27,1	23,5	7,4

Table 6. Values of Total Acidity Production (TAP), Neutralisation Potential (NP) and net neutralisation potential (NNP)

If we consider the average NP:TAP ratio at the Podlipa dump-field (7.4; tab. 6), the risk of the AMD formation is beyond possibility. Such a high average NP:TAP ratio is caused only by value from the dump of the Empfängnis adit (NP:TAP = 135.6). If this only extreme value will be excluded, the NP:TAP ratio will change to 1.72 and it correspond to the low risk of AMD creation.

3.1.2 Heavy metal sorption on clay minerals and hydrogoethite

Rtg.-diffraction analyse prowed, that the most important potential natural sorbents in studied area are the clay minerals and hydrogoethite – $FeO(OH)\cdot nH_2O$, which are formed during the weathering process of rock-material. The research confirmed, that the clay minerals are represented by illite – $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ and muscovite – $KAl_2(AlSi_3O_{10})(F,OH)_2$, caolinite – $Al_2Si_2O_5(OH)_4$, as well as smectite and chlorite mixture. Illite and muscovite are dominant in all samples. The next important mineral is smectite.

The heavy metal sorption study of clay minerals and hydrogoethite from technogenous dump sediments and the study of the free sorption capacity of these natural sorbents in individual samples is a relatively complex problem and the interpretation of these data is

very confusing. Better reproducibility enable the complex interpretation of the results if the concentrations of the individual elements in technogenous sediment, in clay mineral mixture and in clay fraction after maceration in drainage water (tab. 7) is presented in form of toatal values for each element (tabs. 1 - 4). Such a toatal data enable better understand the studied processes and trends.

Sample	Fe	Cu	Pb	Zn	Cd	Bi	Co	Ni	As	Sb	Ag	Cr	Sn
	$\mu g.l^{-1}$												
V-1	486	9864	12	189	0,3	2,1	44	23	15	8,4	0,1	8	0,2

Table 7. ICP-MS analyse of drainage water used for 14 days maceration of clay fraction

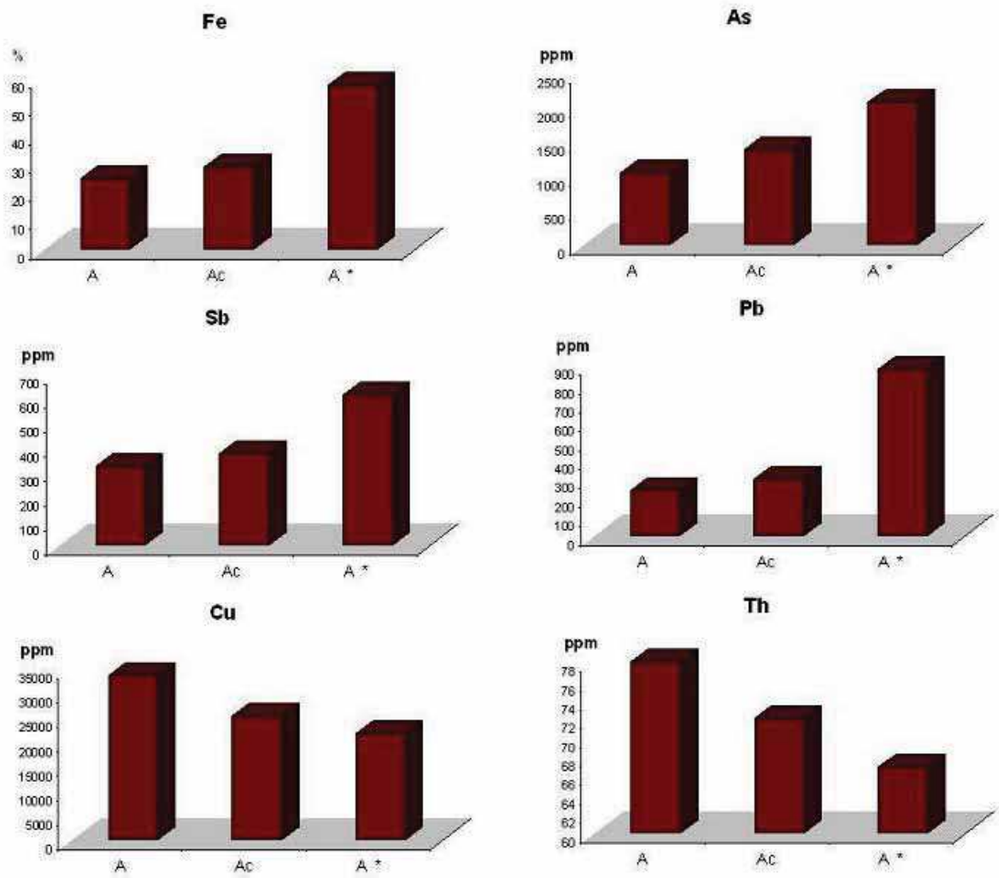

Fig. 8. Toatal content of Fe, As, Sb, Pb, Cu and Th in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (A*).

Preferential sorption of Cr and Th on surface of clay minerals in comparison with hydroghoethite was described. On hydrogoethite surface are preferentially fixed Cu, Zn (± Fe, Cd, Co). The following elements: Sb, Sn, Pb, Ag, Ni, As and U show no legible trends of preferred sorption both on clay minerals and on hydrogoethite rich rock (tabs. 1 - 4).

The following heavy metals: Fe, As, Sb, Ag, Pb, Zn, Bi and U show not only good sorption efficiency on clay minerals but also free sorption capacity of the clay fraction. Opposite trend – lower heavy metal content in clay component in comparison with the sediment and metal elements washing during maceration was proved in case of Th and Cu (Figure 8). Co show moderate increase of content in clay minerals but no free sorption capacity was proved. The Cd, Ni, Co, V and Cr behaviour is very complex (Figure 9).

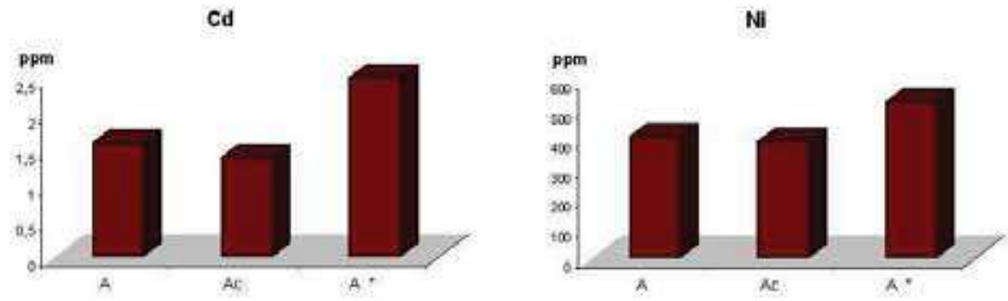

Fig. 9. Toatal content of Cd and Ni in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (A*).

Cd, Ni and V are preferentially fixed in sediments, lower Cd, Ni and V contents are in clay fraction but the clay mineral mixture proved a good ability to fix the mentioned heavy metals (Cd, Ni and V) on their surface (Figure 9). The probable reason of this behaviour is the fact, that the Cd, Ni and V majority is bound in the solid phase and only with difficulties create soluble forms, so in consequence of this behaviour in weathering process are the autochtonous clay minerals insufficiently saturated by V. The same trend was described for Cd, Ni, V and Co in case of hydrogoethite. The Cr behaviour is very similar, only with this difference that while V concentrations are in macerated clay higher as in the original sediment, the Cr concentrations are the highest in the original sediment.
The most complex relations were recognized in the case of Co.
The highest Th content was described in sediments and in soil. The Th contents in clay minerals are lower as in the sediment and after maceration is Th washed out from the clays. This trend is noticeable because in general is U considered to be more mobile as Th. The better mobility of U at the Ľubietová deposit where the content of Th in soil is several times higher as the content of U, while in plants are the contents both of U and Th in consequence of better U mobility approximately identical. The Th/U rate is about 1 : 1.

3.2 Plant contamination by heavy metals

The plants adapted to the specific conditions of the different zones of the studied area show different level of the contamination in individual tissues (roots, twigs/stems, leafs/needles or in flowers/fruits). The article presents also results of the plant tissue degradation study in heavy metal contaminated conditions and compare them with those from reference sites.
The knowledge of content of heavy metals in plants is important from the point of food cycle contamination. The intensity of plant contamination by heavy metals is necessary to critize depending up plant species.

Plant	Sam-ple	Part of the plant	Fe	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
			ppm									
Betula pendula	LB-7	a	91.7	7.1	16.80	24.1	0.02	0.08	5.80	0.90	2.14	2.90
		b	158.5	6.6	16.70	18.6	2.90	0.04	3.50	0.70	1.50	0.30
		b_2	308.9	8.6	71.30	75.6	16.90	0.15	10.70	6.70	0.50	0.10
		c	380.0	25.3	35.40	3.8	8.20	0.08	10.90	3.40	1.29	0.14
Quercus petraea	LB-100	a	274.6	9.2	59.00	57.1	40.10	0.10	11.80	3.50	0.50	0.25
		b	204.1	0.0	41.70	4.7	2.04	0.10	4.70	1.00	0.64	0.09
		c	85.2	8.1	10.30	28.6	30.30	0.06	3.70	1.00	0.77	0.11
		d	210.0	6.5	14.60	17.1	0.02	0.05	3.00	1.10	0.37	0.07
Pinus sylvestris	LB-103	a	156.8	28.1	15.00	14.5	0.70	0.03	2.70	2.30	0.42	0.50
		b	164.6	2.9	15.70	32.2	3.04	0.03	2.50	1.30	0.56	0.13
		b_2	143.0	0.0	16.70	20.5	0.10	0.03	2.30	1.10	0.62	0.11
		c	148.5	59.9	44.30	38.3	8.00	0.10	4.90	2.50	0.15	0.04
		d	95.4	6.8	12.80	15.2	0.04	0.03	2.70	1.60	0.41	0.10
Picea abies	LB-14	a	221.8	7.5	32.40	38.6	0.07	0.07	6.10	6.10	3.14	0.53
		b	158.2	12.1	16.05	2.0	0.82	0.04	9.20	0.80	0.59	0.12
		b_2	-	-	-	-	-	-	-	-	0.19	0.12
		c	134.1	10.1	14.60	1.9	0.70	0.03	9.20	0.80	0.85	0.19
Abies alba	LB-8	a	125.2	10.8	22.14	15.4	3.10	0.06	6.20	1.25	0.49	0.96
		b	221.6	8.0	27.70	15.5	1.40	0.05	5.40	1.80	1.34	0.34
		c	73.2	8.7	8.70	31.5	20.80	0.04	5.42	1.60	2.24	1.14
Juncus articu-latus	LB-1	a	358.0	37.2	85.10	51.4	225.1	0.20	10.20	8.70	19.70	1.52
		b	209.4	70.1	33.20	37.9	4.70	0.10	4.90	2.60	1.40	1.67
		c	208.0	68.3	32.01	35.9	4.00	0.10	4.92	2.55	1.28	1.60
		d	-	-	-	-	-	-	-	-	3.64	0.44
Mentha longifolia	LB-112	a	246.0	100.4	23.30	16.0	0.20	0.06	4.70	1.20	0.57	0.21
		b	89.4	14.3	13.10	11.4	0.04	0.04	2.40	0.50	0.05	0.08
		c	593.6	173.3	38.30	41.2	2.40	0.10	7.60	3.30	0.76	0.26
		d	-	-	-	-	-	-	-	-	1.44	2.07
Salix fragilis	LB-2	a	415.6	63.5	84.00	6.0	0.20	0.20	13.00	9.70	2.84	0.21
		b	131.3	0.0	20.80	6.3	5.30	0.05	3.70	0.60	0.26	0.15
		c	565.9	0.0	74.10	98.6	0.80	0.20	21.00	6.20	0.52	0.11
Acetosell a vulgaris	LB-13	a	184.0	133.7	22.30	4.6	0.30	0.06	9.40	5.7	17.31	3.46
		b	176.8	72.9	31.10	23.1	7.40	0.08	12.00	7.70	13.08	3.30
		c	701.0	46.5	185.80	135.1	0.38	0.42	36.30	25.60	12.97	3.27

Table 8. Analyses of plant tissues from dump-field Ľubietová – Podlipa Explanations to tab. 8 and 9: a - roots; b - live branches and stems; b_2 - dead branches; c – leaves and needles; d – flowers and fruits

The contents of the heavy metals in plant tissues decrease in the following rank: Fe, Zn, Pb a Cu. The comparison of additive concentrations of heavy metals in individual types of plant tissues (roots. branches/stems and leaves/needles) was realised to obtain more complex contamination model of the plant tissues. The comparison was performed with the following wood species and herbs: *Betula pendula. Quercus petraea. Picea abies. Abies alba, Pinus sylvestris. Juncus articulatus. Mentha longifolia*. The study showed (Figure 10) that the highest concentrations of Fe, Pb, As, Sb and Zn were determined in root system. Cu

contaminates leaves and needles in preference. Fe probably enters leaves and needles up to certain concentration level in preference. When this concentration level is exceeded. Fe accumulates in root system after it cannot enter leaves and needles. The contamination of plant tissues of live and dead branches was compared in several plants from the dump-field (*Betula pendula. Pinus sylvestris. Picea abies*) and reference site (*Betula pendula. Quercus petraea*) (tabs. 8 and 9).

Plant	Sample	Part of the plant	Fe	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
			ppm									
Betula pendula	LB-10	a	192.0	2.0	27.10	19.20	0.02	0.06	5.10	2.30	0.31	0.20
		b	107.7	3.5	16.90	14.80	1.30	0.02	3.00	7.70	0.12	0.27
		b_2	108.8	5.6	41.30	75.60	1.90	0.12	1.70	6.70	0.20	0.05
		c	209.0	6.9	25.50	3.10	5.40	0.07	4.70	1.80	0.14	0.04
Quercus petraea	LB-9	a	174.2	4.2	32.00	31.10	0.08	0.06	7.82	1.53	0.35	0.19
		b	67.1	0.0	25.40	2.00	0.02	0.04	3.40	1.80	0.06	0.04
		b_2	158.6	3.2	36.30	30.40	0.20	0.06	3.80	1.00	0.63	0.07
		c	123.2	3.1	27.50	22.20	0.05	0.03	2.80	1.30	0.16	0.09
Pinus sylves- tris	LB-101	a	111.1	8.1	10.20	10.80	0.05	0.02	2.00	2.00	0.16	0.51
		b	84.0	0.0	12.80	11.40	1.20	0.02	2.20	0.30	0.04	0.03
		c	136.8	6.6	22.90	17.00	0.10	0.06	4.50	1.30	0.13	0.06
Picea abies	LB-102	a	121.6	4.5	22.40	28.60	0.04	0.05	4.11	4.10	0.33	0.52
		b	95.2	8.1	10.20	1.15	0.55	0.60	7.10	5.10	0.07	0.06
		c	90.8	7.4	10.01	1.11	0.48	0.52	7.00	4.20	0.17	0.08
		d	84.1	2.1	8.63	0.98	0.60	0.02	8.20	0.70	0.57	0.16
Abies alba	LB-113	a	98.1	3.4	19.70	10.00	0.80	0.04	5.13	1.11	0.39	1.20
		b	112.8	4.6	20.00	11.80	0.80	0.04	4.30	1.40	0.07	0.03
		c	41.7	3.0	17.20	22.40	3.50	0.03	4.90	0.70	0.15	0.11
Juncus articu-latus	LB-114	a	199.5	34.1	39.50	4.30	0.20	0.08	5.10	1.00	0.59	0.18
		b	103.2	8.8	42.90	15.40	0.50	0.05	3.00	1.30	0.16	0.07
		c	100.4	8.0	38.12	15.41	0.49	0.03	2.99	1.30	0.17	0.05
		d	-	-	-	-	-	-	-	-	0.31	0.06
Mentha longi-folia	LB-101	a	246.0	100.4	23.30	16.00	0.20	0.06	4.70	1.20	0.57	0.21
		b	89.4	14.3	12.10	11.40	0.04	0.04	2.40	0.50	0.05	0.08
		c	593.6	173.3	38.30	41.20	2.40	0.10	7.60	3.30	0.76	0.26
		d	-	-	-	-	-	-	-	-	1.44	2.07

Table 9. Analyses of plant tissues from the reference site Ľubietová – Podlipa

3.2.1 Plant tissue defects

Plants at the mine waste dumps have lack of organic nutrients and moisture besides higher concentrations of heavy metals. They mainly populate depressions or weathered parts of the dumps. Permanent plants prevail at the old mine waste dumps. Annual and biennial plants are rare.

Changes of pH and oxidative-reductive potential affect the release and precipitation of heavy metals. It causes the heavy metals transfer into the bottom sediments, solution or soil/rock environment. Bowen (1979) states that Ag, As, Cd, Cu, Pb, Sb and Zn metals have the tendency to accumulate in the upper soil horizon due to vegetation recycling, atmospheric deposition and adsorption by organic mass.

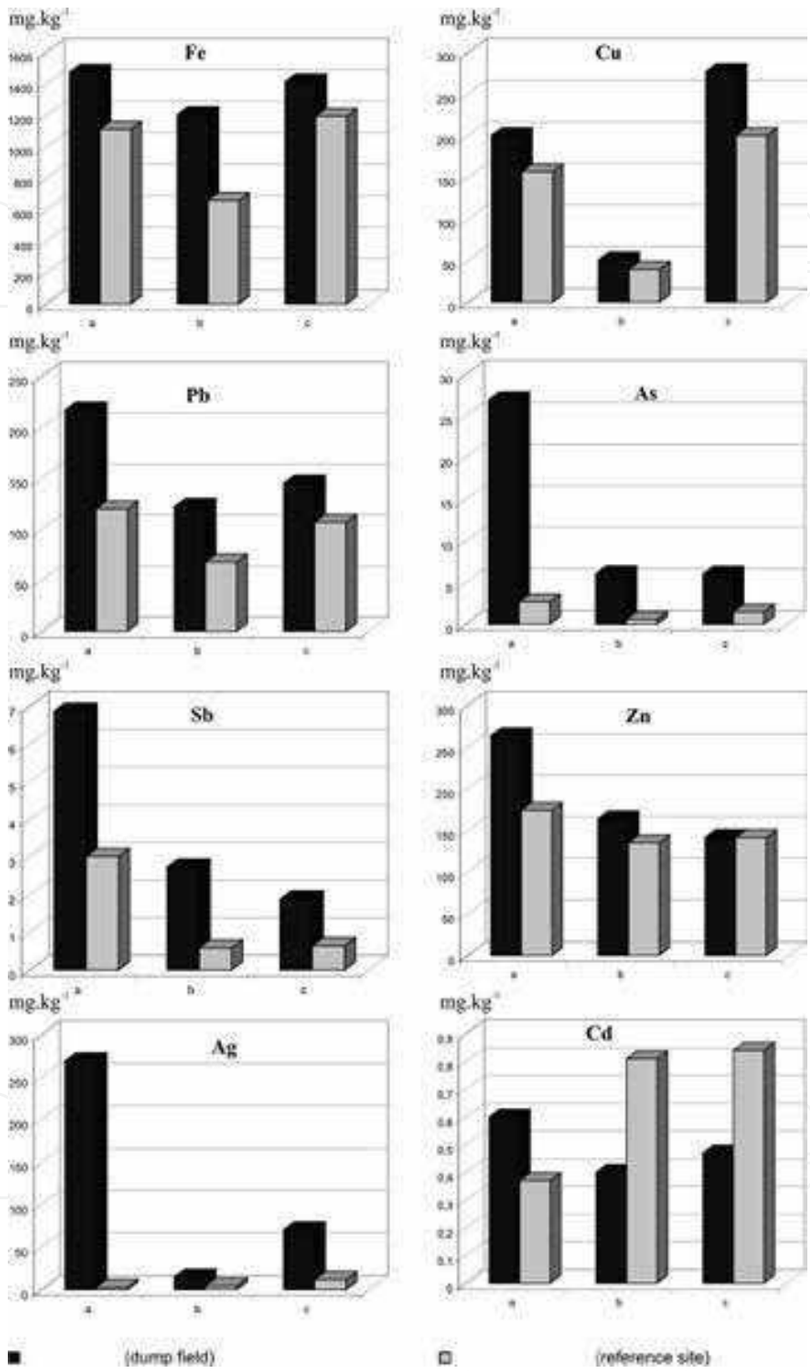

Fig. 10. Additive heavy metal concentrations in individual types of plant tissues
a - roots b - twigs/stems, c- leaves/needles

Fe, Co and Ni metals usually accumulate in higher concentrations in dislocated clay minerals and autigene sesquioxides in lower horizon of the soil profile enriched in clay and oxyhydroxide components.

Year shoots in live branches of *Betula pendula* and *Pinus sylvestris* (Figure 11) from the dump-field are narrow (10/100 μm vs. 2000 μm wide year shoots from the reference area, Figure 12)

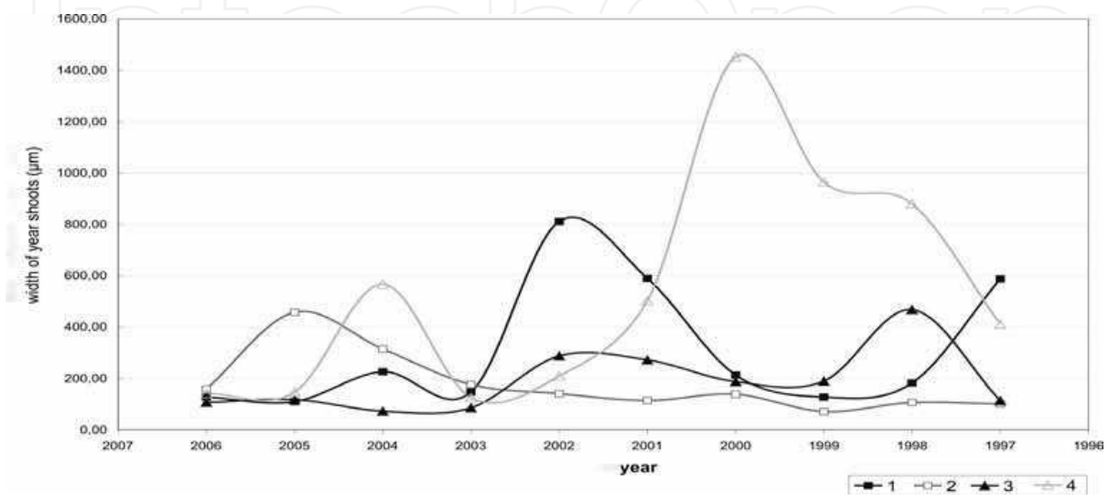

Fig. 11. Comparison of the current year shoots in analysed samples of the *Pinus sylvestris* from the dump-field: 1 - living twig, 2 – dead twig and from reference site: 3 – living twig, 4 – dead twig.

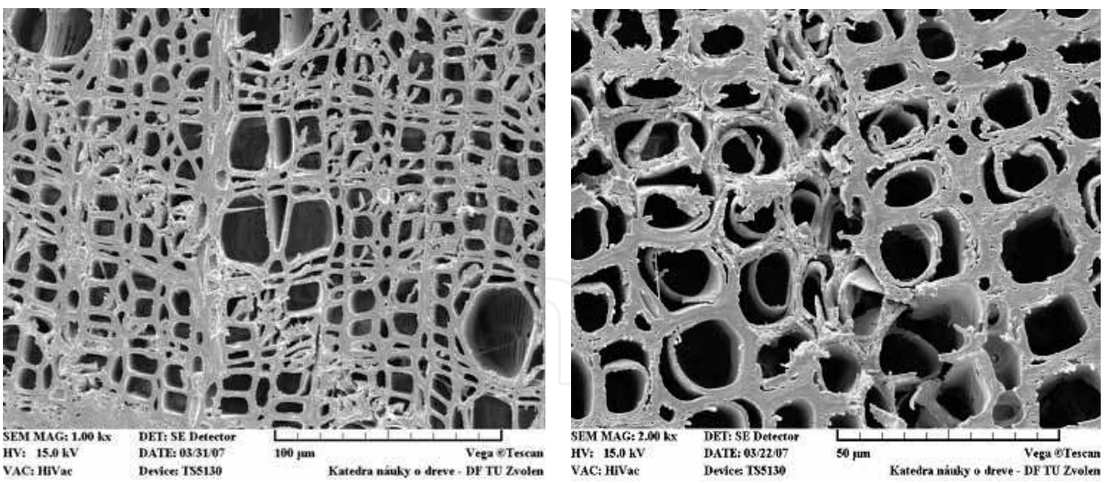

Fig. 12. *Betula pendula:* formation of extraordinary tight current year shoots.

Fig. 13. *Pinus sylvestris*: exfoliation of summer tracheide cell-wall layers.

Anomalous cell-wall exfoliation (Figure 13) and coarsening, occurrence of calluses, zonal occurrence of thick-walled fibres (Figure 14), formation of traumatic resin canals (Figure 15) and numerous hyphaes in vessels (Figure 16) as well as the absence of cell-wall coarsening

suggest defense mechanism of plants which are exposed to the stress factors at the dump-field such as contamination by heavy metals, soil and moisture deficiency, movement of incohesive material down to slope.

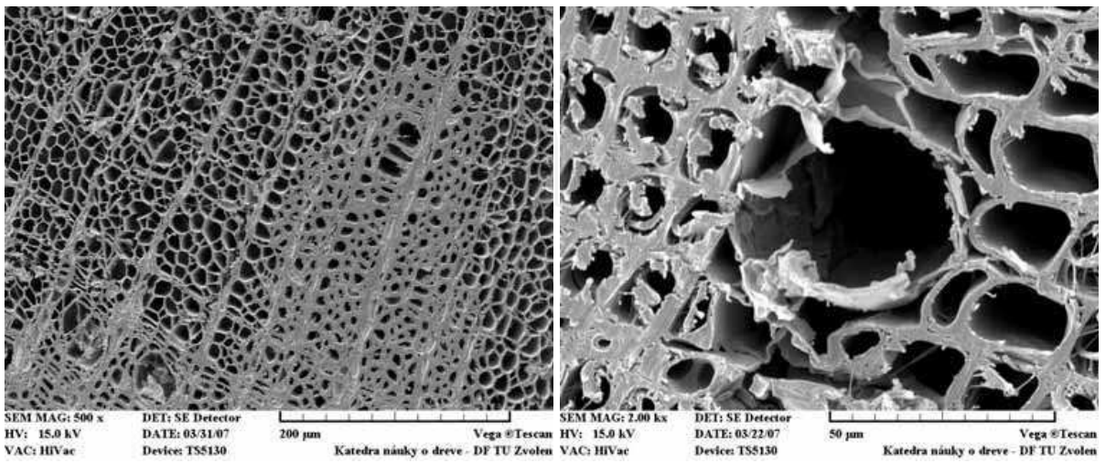

Fig. 14. *Betula pendula*: zonal occurrence of thick-walled fibres.
Fig. 15. *Pinus sylvestris*: formation of the traumatic resin chanals in closeness to the calluses.

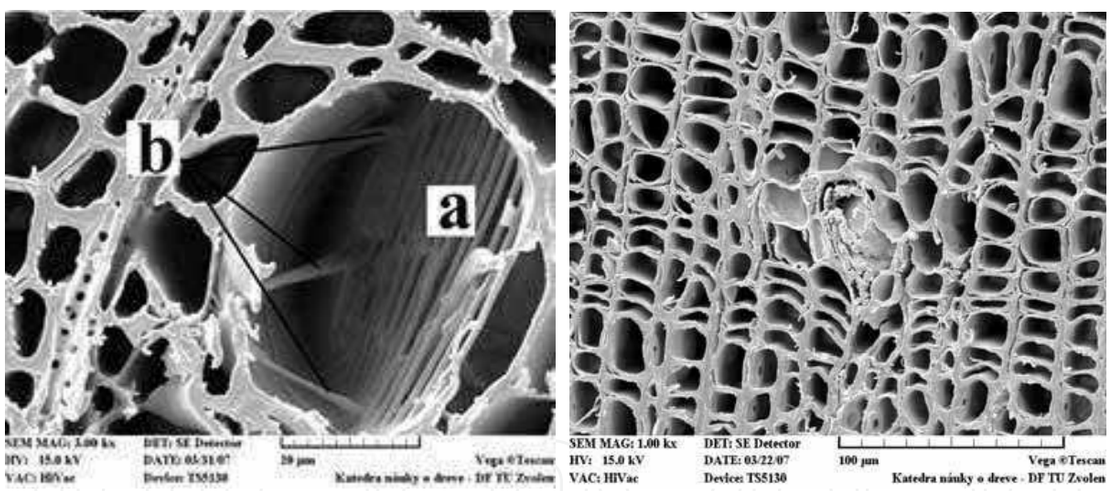

Fig. 16. *Betula pendula*: a – scalar perforation in vessels.. b – hyphaes
Fig. 17. *Pinus sylvestris:* absence of the cell-wall coarsening.

Plant contamination by Fe causes the atrophy of plant tops and the root coarsening. It has been observed by *Picea abies* where the deformation of tree tops and the formation of „stork nests" has been occurred. Plant contamination by Cu causes the formation of dead stains on lower leaves at steam, purple and violet stem coloring (*Acetosella vulgaris*), atrophy of the root system and leaf chlorosis with green veining.
The flora loading by Zn causes the abundant occurrence of plants with leaf chlorosis with green veining (*Picea abies, Betula pendula*), dead stains on leaf-tips (*Acetosella vulgaris*) and rudimentary root system (*Picea abies*). Plant loading by Ni and Co causes the formation of white stains. White stains were described by *Salix fragilis*. Plants receive Cd mostly by roots

in Cd^{2+} form by diffusion due to metal chelatation by organic acids secreted by plant root system. The highest Cd contents are in roots, lower in leaves and then in stems and fruits. The lowest Cd contents are in seeds.

Higher Cd contents cause several diseases such as leaf chlorosis, root darkening and formation of violet-brown stains on leaves. Diseases have been observed at the studied locality by *Picea abies* (needle chlorosis), *Quercus petraea* (root darkening), *Acetosella vulgaris* (formation of violet-brown stains on leaves). Shedding of leaves and needles is present frequently as well. Lack of Cd causes increase of biomass formation. High Cd content causes unproportional growth of leaves and roots, cell extension and stagnation of cell division. For instance, needle length is ultra small by *Pinus sylvestris* (2 cm) at the mine waste dumps.

3.3 Heavy metals in the water

The surface water in the creek draining the valley along the dump-field is gradually contaminated by heavy metals from leached from the technogenous sediments of the mining dumps. The drainage water contains relatively high Cu (up to 2060 $\mu g.l^{-1}$), Fe (up to 584 $\mu g.l^{-1}$), Zn (up to 35 $\mu g.l^{-1}$) and sometimes also Co (up to 10 $\mu g.l^{-1}$) and Pb (up to 5 $\mu g.l^{-1}$) concentrations. The highest As concentration is 6.11 $\mu g.l^{-1}$.

Sam-ple	pH	Eh (mV)	Mn	Zn	Cd	Co	Cu	Fe	Ni	Pb	Sb	As
			$\mu g.l^{-1}$									
V-1a	6.5	-6	<1	<10	0.04	1.1	2.2	26	4.1	4.2	0.74	<1.0
V-1b	7.5	-58	<1	<10	0.05	2.2	2.7	73	5.9	4.3	<1.00	<1.0
V-1c	6.5	-8	11	<10	<0.05	<1.0	5.1	94	1.2	<1.0	1,03	<1.0
V-2b	6.7	-14	<1	<10	0.13	<1.0	42.1	584	2.1	3.0	<1.00	1.69
V-2c	6.9	-21	<1	<10	0.09	<1.0	38.2	580	1.6	2.9	<1.00	1.54
V-3a	6.7	-12	<1	30	0.04	7.0	1 810	86	3.2	2.2	1.12	<1.00
V-3b	6.1	14	<1	40	0.05	9.6	2 060	101	4.9	2.8	1.88	3.41
V-3c	6.5	0	21	<10	<.05	7.6	1 980	45	8.5	2.8	2.35	1.14
V-4a	6.7	-14	<1	<10	0.06	3.1	22.2	263	2.1	4.2	1.72	<1.0
V-4b	6.2	14	<1	<10	0.06	8.1	1 850	274	5.6	3.6	1.57	1.21
V-5a	6.2	-11	<1	<10	0.06	5.5	6.0	170	6.0	4.8	1.66	2.79
V5b	6.3	-8	7	20	0.08	8.3	7.9	210	7.1	5.1	2.21	3.21
V-5d	6.2	-7	4	30	0.07	6.6	8.1	160	8.1	1.0	2.00	1.08
V-6a	7.6	-62	<1	30	0.07	1.9	30.4	270	4.3	3.2	2.00	6.02
V-6b	7.1	-62	<1	32	0.07	2.2	34.8	263	5.0	3.4	2.01	6.11

Table 10. Atom absorption spectrometric analyses of surface water. Expanations: Samples marked by index „a" - rainy period (June 14th 2006), samples marked by index „b" - dry period (February 25th 2007), samples marked by index „c" - rainy period (March 31st 2008), samples marked by index „d" - dry period (May 27th 2008)

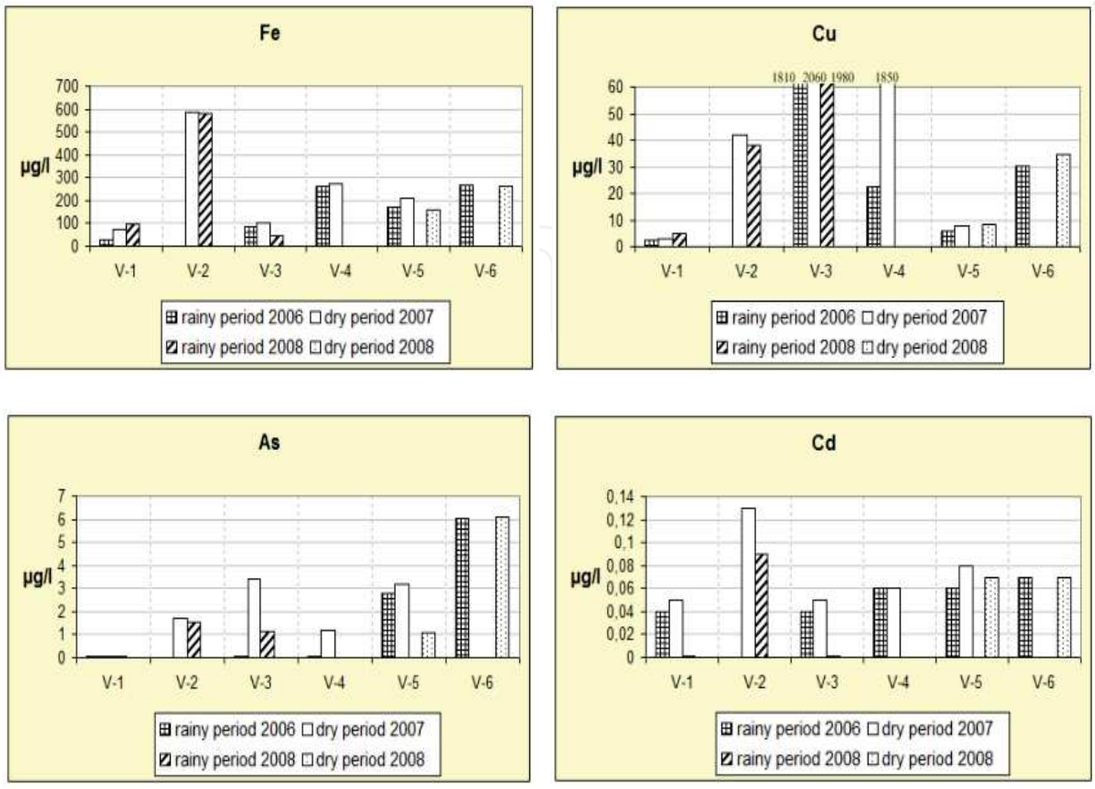

Fig. 18. Comparison of Fe, Cu, As and Cd contents during dry and rainy seasons

Sam -ple	pH	Eh (mV)	Fe	Ni	Mn	Zn	Cu	Cd	Pb	Bi	As	Sb
			µg.l^{-1}									
G-1a	6.55	-4	11	1.1	<5	<10	22.0	<0.05	<1.1	1.36	<1	<1.0
G-1b	6.63	-10	17	1.2	<5	<10	1.3	<0.05	1.9	1.55	<1	<1.0
G-2a	6.72	-14	366	1.3	18	<10	3.0	<0.05	1.3	<1.00	<1	<1.0
G-2b	6.23	-16	210	1.5	8	<10	2.2	<0.05	<1.0	<1.00	<1	<1.0
G-3a	6.85	-21	146	<1.0	15	61.0	14.0	0.13	3.4	<1.00	5	1.42
G-3b	6.55	-23	120	<1.0	17	350.0	5.9	0.1	3.3	<1.00	1.52	1.21
G-4a	6.40	+4	380	5.0	20	<10	30.0	0.5	<1.0	<1.00	1.98	<1.0
G-4b	6.48	-2	2 260	<1.0	55	<10	181	82.0	<1.0	<1.00	2.52	<1.0

Table 11. Atom absorption spectrometric analyses of groundwater (samples G-1, G-2 and G-3) and mineral water (sample G-4). Explanations: a – sampled on March 31st 2008 during the rainy period; b - sampled on May 27th 2008 during the dry period

The heavy metal content in the water is in most cases higher during the dry period in comparison with the rainy period (Figure 18). The As content both in the surface (and drainage) as well as in the groundwater is not high (6.11 µg.l^{-1}). The speciation of the As proved only the presence of the less toxic As^{5+}. The more toxic inorganic As^{3+} is not present.

The presence of *Acidithiobacteria* or of sulphate reducing bacteria was not proved. The acidity both of the surface and groundwater is close to neutral pH (6.4 – 7.6) so the formation of acid mine drainage water is not probable.
The most contaminated is the mineral water from the spring Linhart (Figure 1). The total radioactivity is 6,498 Bq.l^{-1} and the Fe (380 µg.l^{-1}), Cu (181 µg.l^{-1}), Pb (1 µg.l^{-1}) and Cd (82.0 µg.l^{-1}) content substantionally exceed the Slovak decrees No. 296/2005, No 354/2006 Coll.
Precipitation of cementation copper on iron sheets immersed in sink, situated in field-depression beneath the dump of the Empfängnis adit (Figure 1) was described. The contents of selected heavy metals in the Cu-rich drainage water from the sink are documented at tab. 7. Native copper of high fineness (up 96.07 % Cu) on the iron sheets surface was precipitated (Figure 19) after two months of maceration.

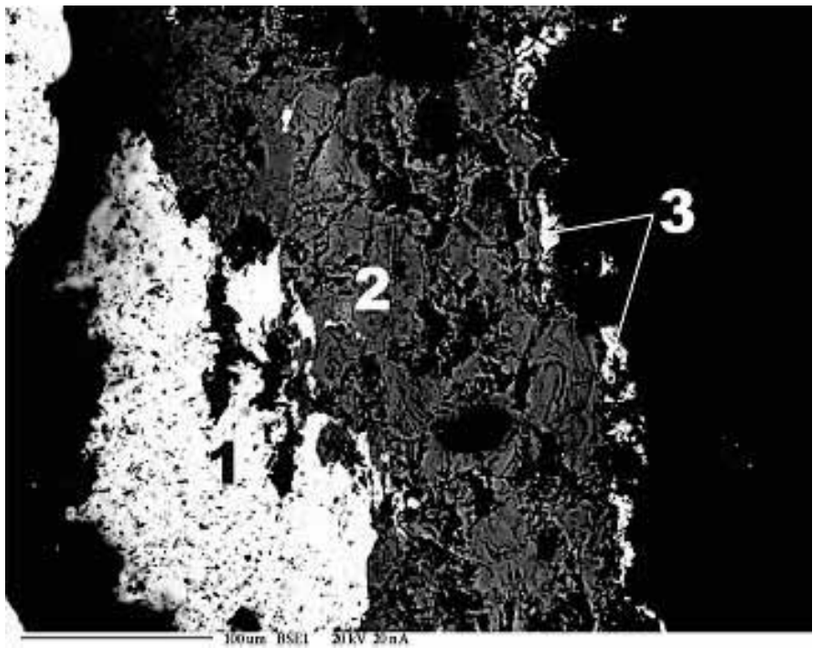

Fig. 19. Native copper (3), the Fe-oxides and Cu-carbonates (2) on the iron surface (1) were precipitated after two months of maceration.

The ability of the drainage water precipitate cementation copper on the iron surface give possibility to realize Fe^0-barrier for elimination of heavy metals from the drainage water and contribute to the remediation of the mining country.

3.4 Laboratory testing of the Fe^0-barrier

The testing of Fe^0-barrier was realised under laboratory conditions using Fe chips and granules (Aldrich) in mixture with dolomite (to avoid colmatage) in rate 9 : 1. The water containing heavy metals percolated hrough the agents 5 hours. Content of all studied metals decreased most intensively during the first two hours of the experiment (Figure 20) when the pH ranged from 6,3 to 8,11 (Figure 21). During the next hours was described already only sorption of Cd and Zn. The most effective was the As sorption (99,97%). Also the Cu sorption (98,98%) and Zn sorption (98,13%) was satisfactory. The effectivity of Cd sorption

(99,64%) is with respect to the relatively low primary Cd content in the drainage water (tab. 7 and 10) also acceptable. The experiment proved the possibility to remove from the water (using dolomite as calcination agent) together with Cu, As, Cd and Zn also Fe (which is during the cementation released to solution).

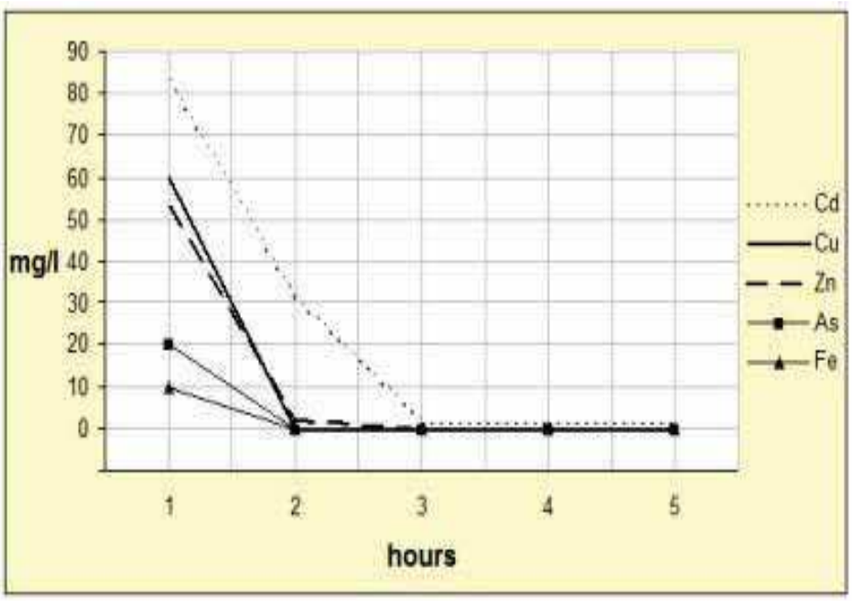

Fig. 20. Fe^0-barrier testing; Decreasing content of the heavy metals during the experiment

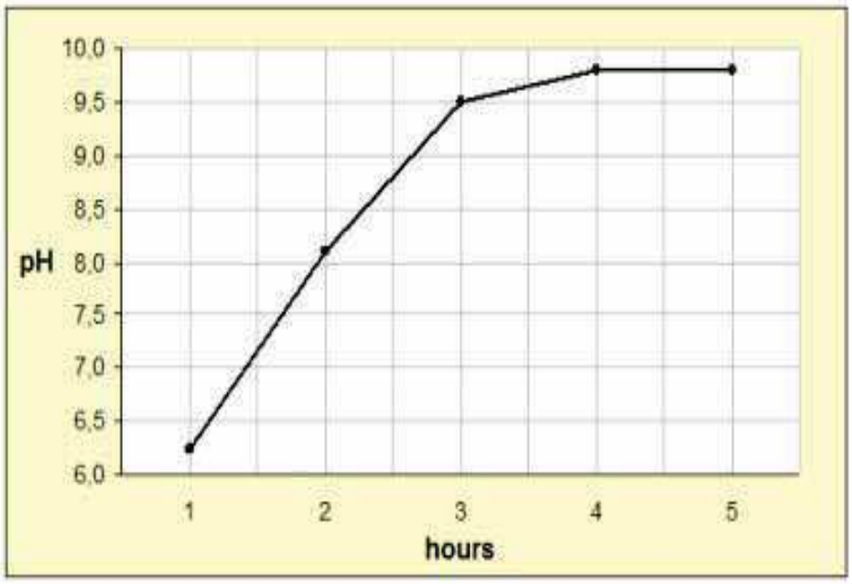

Fig. 21. Fe^0-barrier testing; pH changes during the experiment

4. Conclusion

The dump-field mining sediments are influenced by heavy metals from the hydrothermal Cu-mineralisation. The main contaminants: Cu (up to 20 360 ppm), Fe (up to 2.58 %), As (up to 457 ppm), Sb (up to 80 ppm) and Zn (up to 80 ppm) are accompanied also by U (up to 10 ppm) and Th (up to 35 ppm). The present natural sorbents are predominantly the clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals are good sorbents of V, Cr, Ti, W, Zr, Nb, Ta a Th and at the hydrogoethite of Cu, Zn, Mo, Mn, Mg, (± Fe, Cd, Co, Ca). In the case of the Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi, U was proved also the free sorption capacity.

The paste or rinse pH of sediments measured in distilled H_2O is around 5.3 and only very few samples account acid values (< 5.0). The measuring of the pH paste in the samples using solution of 1M KCl give similar values. It means that only several few samples show markedly acid reaction. The acidity production (AP) vary from 0.625 to 10.31 (in average 3,7) and the neutralization potential (NP $CaCO_3$) from 0.66 to 12.71 $kg.t^{-1}$ (in average cca 27,1 $kg.t^{-1}$ $CaCO_3$). The value of the net neutralisation potential (NPP) and the NP : AP ratio show that the potential of the acid mine drainage water formation is very limited (NPP = 1,42; NP : AP = 1,72) and the environmental risk is negligible.

The surface water (and drainage water) as well as the groundwater water are substantially contamined predominantly by Cu, Fe and As. Both the As content and its speciation don't pose acute risk (the highest arsenic content is only 6.11 $\mu g.l^{-1}$ and it is present only in the form of moderately toxic inorganic As^{5+}). The only risk poses the spring of the mineral water Linhart because of the high radioactivity and high Fe, Cu, Cd and Pb contents. For this reason was the spring closed and it is not used for drinking.

The concentrations of the heavy metals in plant tissues decrease seriately in rate: Fe, Zn, Pb and Cu. Comparison of individual types of plant tissues show that the highest concentrations of heavy metals are in roots, than in leaves and stems and the lowest concentrations are in flowers, seeds and in fruits. The plant tissues from the dump-field are heavily damaged and the growth of the current year shoots are extraordinary tight. The results of the research document the plant defense reactions under the influence of stress factors at the dump sites (absence of soil and water, the heavy metal contamination, mobility of the cohesionless slope material).

The ability of the drainage water precipitate cementation copper on the iron surface give possibility to realize Fe^0-barrier for elimination of heavy metals (Cu, As, Zn, Cd) from the drainage water and contribute to the remediation of the mining country. Application of the dolomite enable remove from the water also the Fe released during the cementation process to solution.

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This book, edited by the Intech committee, combines several hotly debated topics in science, engineering, medicine, information technology, environment, economics and management, and provides a scholarly contribution to its further development. In view of the topical importance of, and the great emphasis placed by the emerging needs of the changing world, it was decided to have this special book publication comprise thirty six chapters which focus on multi-disciplinary and inter-disciplinary topics. The inter-disciplinary works were limited in their capacity so a more coherent and constructive alternative was needed. Our expectation is that this book will help fill this gap because it has crossed the disciplinary divide to incorporate contributions from scientists and other specialists. The Intech committee hopes that its book chapters, journal articles, and other activities will help increase knowledge across disciplines and around the world. To that end the committee invites readers to contribute ideas on how best this objective could be accomplished.

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